A Convenient Synthesis of Optically Active Unhindered Aliphatic Alcohols with High Optical Purity from Non-Racemic β-Hydroxy Sulfides

Byung Tae Cho* **and Dong Jun Kim**

Departmet of Chemistry, Hallym University, Chunchon 200-702, Korea
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A general route for the synthesis of optically active unhindered aliphatic alcohols, where the steric demands between two alkyl groups adjacent to the carbinol are similar, with high enantiomeric purity has been developed by sulfoxifation of chiral β-hydroxy sulfides, followed by alkylation and desulfurization.

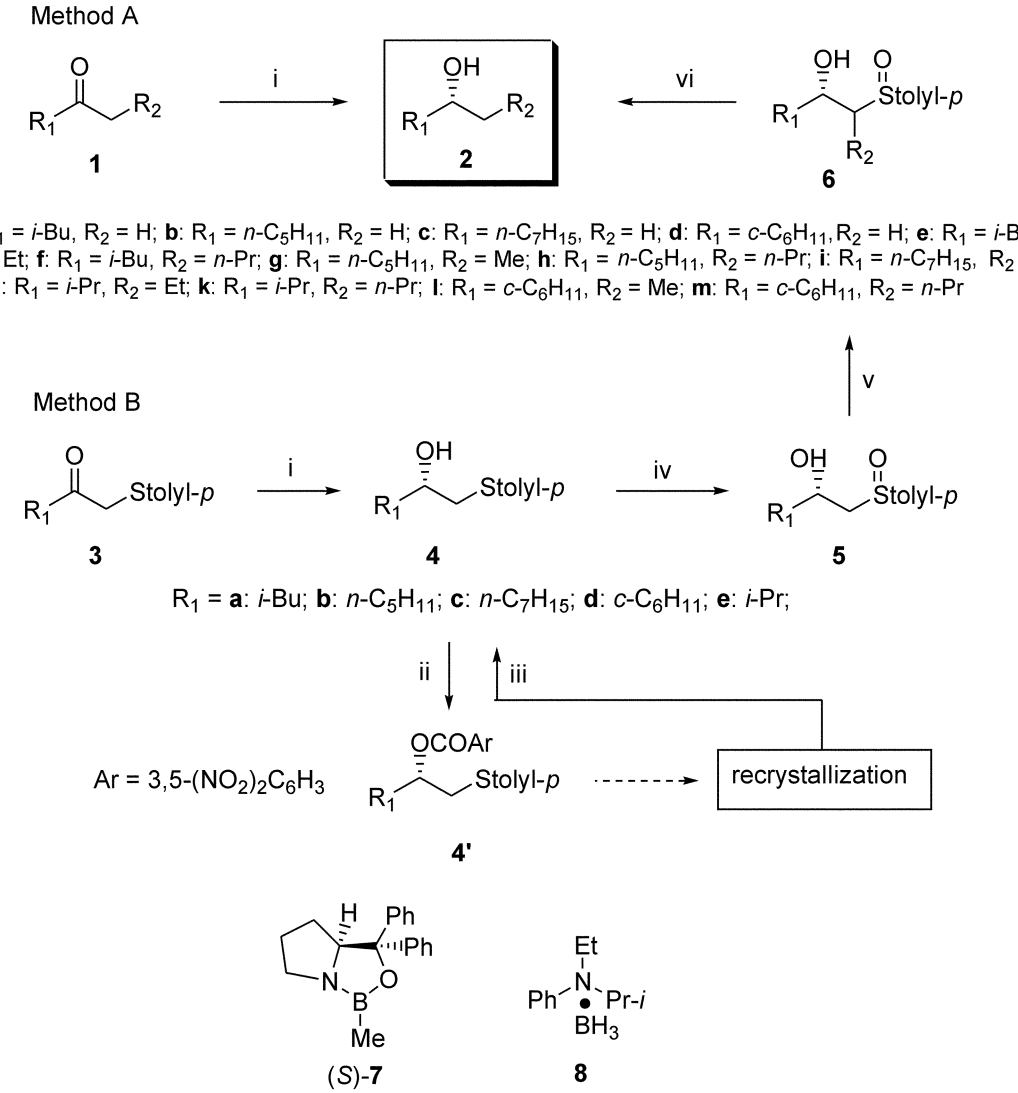
Key Words : Chiral aliphatic alcohols, Asymmetric reduction, (S)-CBS oxazaborolidine, Chiral β-hydroxy sulfides

Introduction

Some optically active unhindered secondary aliphatic alcohols are extremely important as naturally occurring biologically active substances. For examples, optically active 3-octanol,[1] 2-methyl-4-heptanol,[2] 2-methyl-4-octanol,[2] 2-dodecanol[3] and acetates of 2-tridecanol[4] and 2-pentadecanol[5] are founded as their pheromones in various species of the insect kingdoms, such as *Myrmica scabrinodis*, *Crematogaster castanea*, *C. liengmei*, *C. auberti*, *Metamasius hemipterus*, *Drosophilia mulleri*, and *Drosophilia busckii*. One of the simplest methods for obtaining these alcohols may be asymmetric reduction of prochiral ketones. A variety of highly efficient catalytic and stoichiometric asymmetric reducing agents for the reduction of prochiral ketones have been extensively reported.[6] However, most of these reagents provided high enantioselectivity for aryl or hindered alkyl methyl ketones (R = aryl, *t*-Bu, or cyclohexyl in RCOMe) where there is enough steric bias. Quite rare success has been published for the reduction of unhindered dialkyl ketones where the steric demands between two alkyl groups adjacent to the carbonyl are similar. Until now, only few asymmetric reducing agents, namely, NB-Enantride,[7] Eapine-Hydride,[8] and (*R*,*R*)- or (*S*,*S*)-2,5-dimethylborolane,[9] have been successfully used for the reduction. On the other hand, chiral β-hydroxy sulfides and their sulfoxides are widely used as starting materials for the synthesis of a variety of chiral intermediates.[10] Recently we reported the synthesis of non-racemic epoxides and 1,2-diol starting from chiral β-hydroxy sulfides[11] Also, we have successfully achieved the highly enantioselective synthesis of optically active insect pheromones, such as (*R*)- and (*S*)-3-octanol, (*R*)-2-methyl-4-heptanol, (*R*)-2-methyl-4-octanol and (*R*)-2-dodecanol, by sulfoxidation of chiral β-hydroxy sulfides, followed by alkylation and desulfurization.[12] In our continuing programs for applications of oxazaborolidine-catalyzed asymmetric reduction, we developed a general route for the synthesis of optically active unhindered aliphatic secondary alcohols from chiral β-hydroxy sulfides using this methodology.

Results and Discussion

First, we set up our experiments for preparation of three types of dialkyl carbinols $R_1CHOHCH_2R_2$, where R_1 = 1° or 2° alkyl, R_2 = H for type I (runs 1-4, Table 1), R_1, R_2 = 1° alkyl for type II (runs 5-9), and R_1 = 2° alkyl, R_2 = 1° alkyl for type III (runs 10-13). As shown in Scheme 1, we initially carried out asymmetric borane reduction of these types of ketones using (*S*)-CBS-oxazaborolidine (**7**) and *N*-ethyl-*N*-isopropylaniline borane complex (**8**) as catalyst and borane carrier, respectively, which is one of the most promising chiral reducing agents to provide high enantioselection for the reduction of various prochiral ketones[6f] (Method A). For the reduction of ketones in type I, all the reduction examined gave moderate enantioselectivity (60-64% ee) except for the case of cyclohexyl methyl ketone (**1d**) (98% ee) as expected (runs 1-4). In the case of ketones in type II, the reduction of 2-methyl-4-heptanone (**1e**) provided (*R*)-2-methyl-3-heptanol with 18% ee (run 5). The reduction of 3-octanone (**1g**) and 3-decanone (**1i**) afforded the (*R*)-enriched corresponding alcohols with 61% ee and 59% ee, respectively (rune 7 and 9). For the reduction of ketones in type III having a similar steric bias between two alkyl groups afforded low enantioselectivity, such as 2% ee for 2-methyl-2-hxanone (**1j**) (run 10) and 18% ee for cyclohexyl ethyl ketone (**1m**) (run 13). The results are summarized in Table 1. Next, we examined an alternative route of the synthesis of optically active those unhindered aliphatic alcohols using non-racemic β-hydroxy sulfides **4** as starting materials, which are prepared from the **7**-catalyzed reduction of β-keto sulfides according to our previous procedure[12,13] (Method B). The reduction of relatively unhindered β-keto sulfides, such as R_1 = *i*-Bu (**3a**), *n*-C_5H_{11} (**3b**), and *n*-C_7H_{15} (**3c**) in R_1COCH_2S-toly-*p*, provided the corresponding product alcohols **4** with 74-81% ee. In contrast, the cases of R_1 = *c*-C_6H_{11} (**3d**) and *i*-Pr (**3e**) afforded 99% and 88% ee, respectively. Enantiomeric purities of **4** obtained were determined by HPLC analysis using a 25 cm Whelk-O1 or Chiralcel OD-H chiral column. Optical purities of the resulting alcohols with 74-88% ee



a: R_1 = *i*-Bu, R_2 = H; **b**: R_1 = *n*-C_5H_{11}, R_2 = H; **c**: R_1 = *n*-C_7H_{15}, R_2 = H; **d**: R_1 = *c*-C_6H_{11}, R_2 = H; **e**: R_1 = *i*-Bu, R_2 = Et; **f**: R_1 = *i*-Bu, R_2 = *n*-Pr; **g**: R_1 = *n*-C_5H_{11}, R_2 = Me; **h**: R_1 = *n*-C_5H_{11}, R_2 = *n*-Pr; **i**: R_1 = *n*-C_7H_{15}, R_2 = Me; **j**: R_1 = *i*-Pr, R_2 = Et; **k**: R_1 = *i*-Pr, R_2 = *n*-Pr; **l**: R_1 = *c*-C_6H_{11}, R_2 = Me; **m**: R_1 = *c*-C_6H_{11}, R_2 = *n*-Pr

R_1 = **a**: *i*-Bu; **b**: *n*-C_5H_{11}; **c**: *n*-C_7H_{15}; **d**: *c*-C_6H_{11}; **e**: *i*-Pr;

i. (*S*)-**7** (0.1 eq), **8** (1.0eq), THF, 25 °C (99%); ii. 3,5-$(NO_2)_2C_6H_3COCl$ (1.1 eq), TMEDA (1.1 eq), CH_2Cl_2 (94-97%); iii. 2*N* NaOH, MeOH, rt (97-99%); iv. *m*-CPBA (1.0 eq), CH_2Cl_2, rt (91-95%); v. *n*-BuLi (2.8 eq), R'I (1.1 eq), THF, -78 °C (65-85%); vi. Raney Ni, MeOH, rt (89-95%)

Scheme 1

(**4a-c** and **4e**) were improved to 95-98% ee by recrystallization of their 3,5-dinitrobenzoates in appropriate solvents (Table 2). Chiral *β*-hydroxy sulfoxides **5** obtained in 93-96% yield from oxidation of **4** with *m*-chloroperbenzoic acid in dichloromethane were alkylated with MeI, EtI, or *n*-PrI in the presence of excess *n*-BuLi in THF at -78 °C to give the corresponding a-alkylated sulfoxides **6** in 72-90% yield. Finally, treatment of **6** with Raney-nickel in methanol at room temperature[14] provided optically active aliphatic alcohols **2** with high enantioselectvity in 90-93% yield. During sulfoxidation, alkylation and desulfurization, racemization was not observed. It is particularly noteworthy that method B provides very high optically active dialkyl carbinols of type II and III where the steric demands between two alkyl groups adjacent to the carbinol are very similar. Of the chiral aliphatic alcohols obtained, (*R*)-2-methyl-4-hepanol (**2e**) and (*R*)-2-methyl-4-octanol (**2f**) are identified as the male-produced aggregation pheromones of the West Indian sugarcane weevils *Metamasius hemipterus*[2] and (*R*)-3-octanol (**2g**) is the sex attractant pheromone of *Myrmica* scabrinodis.[1]

Conclusions

We have established a general and convenient route for synthesis of optically active aliphatic alcohols, having a similar steric bias between two alkyl groups adjacent to the carbinol group, with very high enantiomeric purity starting from non-racemic *β*-hydroxy sulfides. This methodology was utilized for synthesis of optically active insect pheromones, such as (*R*)-2-methyl-4-hepanol, (*R*)-2-methyl-4-octanol and (*R*)-3-octanol.

Table 1. Preparation of optically active aliphatic alcohols **2**

Type	Run	$R_1CHOHCH_2R_2$ (**2**)		Compd	Method A[a]		Method B[b]			
		R_1	R_2		Yield[c]	% ee	Yield[d]	[α] (*c*, solvent)	% ee	Config.[e]
I	1	*i*-Bu	H	**2a**	97	64[f]	85	g	98[f]	*R*
	2	*n*-C_5H_{11}	H	**2b**	96	60[f]	82	–9.49 (0.95, $CHCl_3$)	96[f]	*R*
	3	*n*-C_7H_{15}	H	**2c**	98	62[h]	85	–6.91 (1.1, $CHCl_3$)	96[h]	*R*
	4	*c*-C_6H_{11}	H	**2d**	98	98[i]	93	+11.59 (2.23, CCl_4)	99[i]	*R*
II	5	*i*-Bu	Et	**2e**	96	18[j]	64	–12.24 (0.4, MeOH)	98[j]	*R*
	6	*i*-Bu	*n*-Pr	**2f**	l		62	–11.95 (0.45, MeOH)	99[k]	*R*
	7	*n*-C_5H_{11}	Me	**2g**	97	61[f]	76	–6.53 (1.21, $CHCl_3$)	96[f]	*R*
	8	*n*-C_5H_{11}	*n*-Pr	**2h**	l		63	–3.17 (0.4, CCl_4)	97[j]	*R*
	9	*n*-C_7H_{15}	Me	**2i**	96	59[h]	66	–8.29 (0.59, $CHCl_3$)	96[h]	*R*
III	10	*i*-Pr	Et	**2j**	94	2[h]	62	+28.2 (0.95, $CHCl_3$	97[h]	*R*
	11	*i*-Pr	*n*-Pr	**2k**	l		56	+25.52 (1.15, EtOH)	97[h]	*R*
	12	*c*-C_6H_{11}	Me	**2l**	98	18[i]	74	+7.23 (0.68, $CHCl_3$)	99[i]	*R*
	13	*c*-C_6H_{11}	*n*-Pr	**2m**	l		67	+14.25 (1.93, $CHCl_3$)	99[h]	*R*

[a]Method A = [**1**] : [(*S*)-**7**] : [**8**] = 1 : 0.1 : 1.0, THF, 25 °C. [b]Method B = The product alcohols **2** were prepared from optically active **4**, see experimental section. [c]Isolated yield. [d]Isolated overall yield from **3**. [e]By comparison with those reported in literature. [f]By GC analysis using chiral G-TA (Astec) column. [g]Not determined. [h]By GC analysis of its acetate using chiral β-Dex (Supelco) column. [i]By GC analysis using chiral α-Dex (Supelco) column. [j]By HPLC analysis of its benzoate using Chiralpak OT (Daicel) column. [k]By comparison of optical rotation value reported. [l]Reaction was not carried out.

Table 2. Preparation of optically active **4**

Before upgrade[a]			After upgrade[b]		
Cpd	Yield (%)	% ee	Yield (%)	% ee	Confg.
4a	98[c]	81[c]	80c	98[c]	*S*
4b	97[c]	74[c]	62c	96[c]	*S*
4c	98	74[d]	80	96[d]	*S*
4e	97	88[c,d]	87	98[d]	*S*

[a][**3**] : [(*S*)-**7**] : [**8**] = 1 : 0.1 : 1, THF, 25 °C. [b]By recrystallization of their 3,5-dinitrobenzoates. [c]Data taken from ref. 12. [d]Determined by HPLC analysis using a Whelk-O1 chiral column.

Experimental Section

General. All operations with air-sensitive materials were carried out under a nitrogen atmosphere in oven-dried glassware. Liquid materials were transferred with a double-ended needle. The reactions were monitored by TLC using silica gel plates and the products were purified by flash column chromatography on silica gel (Merck; 230-400 mesh). NMR spectra were recorded at 200, 300 or 400 MHz for ^1H and 50, 75 or 100 MHz for ^{13}C using Me_4Si as the internal standard in $CDCl_3$. Optical rotations were measured with a high resolution digital polarimeter. Melting points were uncorrected. Enantiomeric excesses (e.e.s) of the products were determined by HPLC analyses using a 4.6 × 25 mm Whelk-O1 (Regis), Chiralpak OT or Chiralcel OD-H (Daicel) chiral column and GC analysis using a 0.25 mm × 30 m α-Dex 120 (Supelco), β-Dex 120 (Supelco) or G-TA (Astec) chiral capillary column.

Materials. Most of organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation when necessary. THF was distilled over sodium benzophenone ketyl and stored in ampules under nitrogen atmosphere. The CBS reagent **7** and *N*-ethyl-*N*-isopropylaniline-borane complex **8** were purchased from the Aldrich Chemical Company, Inc. β-Keto *p*-tolylsulfides **3** were prepared by reaction of 2-halo-1-alkylethanones with the corresponding sodium alkyl or arylthiolates according to the known procedure.[15]

Preparation of 2 Using Method A.

General procedure: To a solution of (*S*)-**7** (0.2 mmol; 0.2 M, 1.0 mL) in THF was added a solution of *N*-ethyl-*N*-isopropylaniline-borane complex **8** (2.0 mmol; 2.0 M, 1.0 mL) in THF. To this was added slowly 2 mL of THF solution of **1** (2 mmol) over a period of 1.5 h using a syringe pump at 25 °C. After the addition, the reaction mixture was stirred for 10 min, quenched cautiously with methanol (0.5 mL), and stirred for additional 30 min. The solvent was evaporated under reduced pressure. The crude alcohols (**2**) obtained were further purified by a flash column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexane (1/4) as eluent. Enantiomeric purities of **2** were determined by GC of HPLC analysis using chiral columns (*vide infra*). The results are summarized in Table 1.

Preparation of 2 Using Method B.

Asymmetric borane reduction of β-keto sulfides (3) using 7 as catalyst: The reduction of **3c** is representative. Using the same procedure, crude (*S*)-(+)-1-(*p*-tolylsulfanyl)-2-nonanol (**4c**) was obtained in nearly quantitative yield. It was further purified by a flash column chromatography on silica gel (230-400 mesh) using ethyl acetate/hexane (1/4) as eluent: R_f 0.42 (EtOAc/hexane 1 : 4); mp 27-28 °C; 97% yield; IR (neat, cm^{-1}): 3417, 2927, 1493, 803; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.26 Hz), 1.25-1.61 (m, 12H), 2.32 (s, 3H), 2.46 (d, 1H, J = 3.36 Hz), 2.78 (dd, 1H, J = 8.85, 13.74 Hz), 3.10 (dd, 1H, J = 3.36, 13.43 Hz), 3.61 (m, 1H), 7.11 (d, 2H, J = 8.24 Hz), 7.31 (d, 2H, J = 7.94 Hz);

^{13}C NMR (50 MHz, $CDCl_3$) δ 14.73, 21.67, 23.27, 26.32, 29.83, 30.21, 32.42, 36.69, 43.62, 69.84, 130.54, 131.57, 132.04, 137.57; Calcd. for $C_{16}H_{26}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 72.13; H, 9.85; S, 12.07; $[\alpha]_D^{20}$ +32.34 (*c* 0.97, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 chiral column [*iso*-PrOH/hexane: 1/99; flow rate: 0.3 mL/min; detector: 254 nm] showed it to be 74% ee [t_R(*S*) 25.90 min and t_R(*R*) 27.96 min]. Optically active β-hydroxy sulfides, such as (*S*)-**4a** with 81% ee, (*S*)-**4b** with 74% ee, (*S*)-**4d** with 99% ee, and (*S*)-**4a** with 88% ee, were obtained from the known method.[13]

Improvement of optical purities of 4a-c and 4e. Using our previous procedure,[12] optical purities of **4c** and **4e** were upgraded by recrystallization of their 3,5-dinitrobenzoates, followed by hydrolysis with 2 *N*-NaOH as follow. To a mixture of **4c** or **4e** (5 mmol) and TMEDA (5 mmol) in dichloromethane (20 mL) was added a solution of 3,5-dinitrobenzoyl chloride (7.5 mmol) in dichloromethane (20 mL) containing 2 drops of THF and the mixture was stirred at room temperature for 12 h. To this was added a saturated $NaHCO_3$ solution (20 mL) with vigorous stirring. Organic layer was separated and then aqueous layer was extracted with dichloromethane (3 × 20 mL). Combined extract was dried over anhydrous Na_2SO_4, filtered and concentrated to give **4'c** or **4'e** in nearly quantitative yields. The esters obtained were recrystallized from ethyl acetate-hexane.

Compound 4'c. 96% yield; light yellow solid; mp 49-50 °C; IR (KBr, cm^{-1}): 2980, 1728, 1545, 1344, 1273, 1167, 1076; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 6.41 Hz), 1.25-1.38 (m, 10H), 2.22 (s, 3H), 3.23 (d, 2H, *J* = 5.8 Hz), 5.36 (m, 1H), 6.97 (d, 2H, *J* = 7.94 Hz), 7.27 (d, 2H, *J* = 7.94 Hz), 8.95 (d, 2H, *J* = 2.14 Hz), 9.18 (t, 1H, *J* = 2.14 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.69, 23.24, 25.92, 29.71, 19.91, 32.35, 34.01, 39.09, 77.49, 122.80, 130.06, 130.48, 131.61, 132.42, 134.55, 137.56, 149.18, 162.71; Calcd. for $C_{23}H_{28}N_2O_6S$: C, 59.98; H, 6.13; N, 6.08; S, 6.96; Found: C, 59.92; H, 6.09; N, 6.19; S, 7.04; Single recrystallizaton of this ester with 74% ee from ethyl ether provided **4'd** with 96% ee in 80% yield; $[\alpha]_D^{20}$ +114.26 (*c* 0.97, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 column [*iso*-PrOH/hexane: 1/9; flow rate: 1.0 mL/min; detector: 254 nm] showed it to be 96% ee [t_R(*R*) 10.96 min and t_R(*S*) 11.91 min].

Compound 4'e. 97% yield; light yellow solid; mp 121-123 °C; IR (KBr, cm^{-1}): 2977, 1734, 1542, 1343, 1271, 1167, 1141; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.01 (d, 6H, *J* = 6.71 Hz), 2.15-2.24 (m, 3H), 3.24 (d, 2H, *J* = 5.8 Hz), 5.22 (q, 1H, *J* = 6.0 Hz), 6.96 (d, 2H, *J* = 7.94 Hz), 7.26 (d, 2H, *J* = 7.94 Hz), 8.95 (d, 2H, *J* = 2.14 Hz), 9.19 (t, 1H, *J* = 2.14 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.40, 19.28, 31.92, 37.08, 81.66, 122.78, 130.01, 130.48, 131.65, 132.42, 134.53, 137.56, 149.18, 162.74; Calcd. for $C_{19}H_{20}N_2O_6S$: C, 56.42; H, 4.98; N, 6.93; S, 7.93; Found: C, 56.43; H, 5.02; N, 6.94; S, 7.96; Single recrystallizaton of this ester with 88% ee from ethyl ether provided **4a** with 97% ee in 87% yield; $[\alpha]_D^{20}$ +153.8 (*c* 1.04, $CHCl_3$), *S*; HPLC analysis using a Whelk-O1 column [*iso*-PrOH/hexane: 1/99; flow rate: 0.8 mL/min; detector: 254 nm] showed it to be 96% ee [t_R(*R*) 15.12 min and t_R(*S*) 16.05 min]. Using the same methodology, optical purities of **4'a** and **4'b** were upgraded from 81% ee and 74% ee to 96% ee and 98% ee, respectively.[12]

Hydrolysis of 4' and sulfoxidation of 4. Preparation of 5.

Hydrolysis of 4': The ester **4'** (5 mmol) recystallized was dissolved in methanol (50 mL), treated with 2 *N* NaOH (50 mL) and stirred for 20 min at room temperature. After evaporation of methanol under reduced pressure, residue was extracted with ethyl ether (3 × 10 mL). The combined extract was dried over anhydrous $MgSO_4$, filtered and concentrated to give **4** in nearly quantitative yields. β-Hydroxy sulfides (**4**) obtained could be used for sulfoxidation (vide infra) without further purification.

Sulfoxidation: To a solution of **4** (4 mmol) in dichloromethane (20 mL) was added dropwise a solution of *m*-chloroperbenzoic acid (4.4 mmol) in dichloromethane (30 mL) for 10 min at 0 °C. After the mixture was stirred for 30 min at room temperature, organic layer was separated, washed with 2 *N* NaOH (2 × 10 mL) and brine (2 × 10 mL), dried over anhydrous $MgSO_4$, filtered and concentrated to give β-hydroxy sulfoxide (**5**), which could be used for alkylation without further purification. The compounds **5a** and **5b** are prepared by the known procedure.[12]

(2*S*)-1-[(*RS*)-*p*-Toluenesulfinyl]-2-nonanol 5c. R_f 0.32 (EtOAc/hexane 1/1); oil; 92% yield; IR (neat, cm^{-1}): 3426, 2931, 1038; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.87 (m, 3H), 1.23-1.68 (m, 12H), 2.43 (s, 3H), 2.65 (dd, 0.45H, *J* = 1.8 and 13.4 Hz), 2.79 (dd, 0.55H, *J* = 2.4 and 13.1 Hz), 2.93 (dd, 0.55H, *J* = 9.2 and 13.1 Hz), 3.02 (dd, 0.45H, *J* = 9.6 and 13.6 Hz), 3.68 (d, 0.55H, *J* = 2.75 Hz), 3.77 (s, 0.45H), 4.15 (m, 0.45H), 4.30 (m, 0.55H), 7.35 (d, 2H, *J* = 7.94 Hz), 7.50-7.58 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.64, 22.15, 23.20, 25.34, 25.43, 32.21, 32.30, 37.65, 37.92, 61.63, 63.05, 67.54, 69.63, 124.69, 130.89, 142.27, 142.74; Calcd. for $C_{16}H_{26}O_2S$: C, 68.04; H, 9.28; S, 11.35; Found: C, 68.10; H, 9.22; S, 11.41.

(2*S*)-3-Cyclohexyl-1-[(*RS*)-*p*-toluenesulfinyl]-2-ethanol 5d. R_f 0.31 (EtOAc/hexane 1/1); mp 77-81 °C; 95% yield; IR (KBr, cm^{-1}): 3422, 2956, 1038; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93-1.81 (m, 11H), 2.43 (s, 3H), 2.69 (dd, 0.49H, *J* = 13.43, 1.53 Hz), 2.80 (dd, 0.51H, *J* = 13.13, 2.14 Hz), 2.99 (m, 1H), 3.68 (d, 0.49H, *J* = 3.66 Hz), 3.78 (d, 0.51H, *J* = 2.14 Hz), 3.94 (m, 0.49H), 4.07 (m, 0.51H), 7.34 (d, 2H, *J* = 7.94 Hz), 7.54 (t, 2H, *J* = 7.94 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.05, 22.00, 26.58, 26.65, 26.73, 26.96, 27.01, 28.46, 28.54, 29.15, 29.29, 44.25, 44.52, 60.31, 61.13, 71.20, 73.52, 125.21, 131.52, 143.21, 143.92; Calcd. for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32; S, 12.04; Found: C, 67.47; H, 8.31; S, 12.12.

(2*S*)-3-Methyl-1-[(*RS*)-*p*-toluenesulfinyl]-2-butanol 5e. R_f 0.19 (EtOAc/hexane 1/1); oil; 93% yield; IR (neat, cm^{-1}): 3433, 2928, 1033; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, 3H, *J* = 4.4 Hz), 0.92 (d, 1.62H, *J* = 1.6 Hz), 0.94 (d, 1.38H, *J* = 1.6 Hz), 1.79 (m, 1H), 2.66 (dd, 0.46H, *J* = 9.0, 1.2 Hz),

2.77 (dd, 0.54H, *J* = 8.8, 1.4 Hz), 2.96 (m, 1H), 3.83 (d, 0.46H, *J* = 2.2 Hz), 3.93 (m, 1H), 4.08 (s, 0.54H), 7.34 (d, 2H, *J* = 5.2 Hz), 7.49-7.56 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 17.81, 18.33, 18.58, 21.93, 34.04, 34.25, 59.56, 71.22, 73.74, 124.19, 130.28, 130.40, 140.65, 142.31; Calcd. for $C_{12}H_{18}O_2S$: C, 63.68; H, 8.02; S, 14.17; Found: C, 63.57; H, 8.08; S, 14.22.

α-Alkylation of 5. General Procedure.[16] Under a nitrogen atmosphere, *n*-BuLi (5.6 mmol, 2.5 M in hexane) was added dropwise to **5** (2 mmol) in anhydrous THF (10 mL) at -78 °C and the mixture was stirred for 30 min at the same temperature. To this, alkyl iodides (2.2 mmol) was added dropwise and the resulting mixture was stirred for 30 min at -78 °C, allowed to warm to 20 °C over 2 h, and then quenched by addition of saturated ammonium chloride (10 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The combined extract was dried over anhydrous Na_2SO_4, filtered and concentrated to give **6**. The crude alkylated products obtained were further purified by a flash column chromatography on silica gel (230-400mesh).

(4*RS*,5*S*)-2-[(*RS*)-*p*-Toluenesulfinyl]-5-decanol 6h. R_f 0.41 (EtOAc/hexane 1/1); oil; 75% yield; IR (neat, cm^{-1}): 3401, 3002, 1037; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.71-1.64 (m, 18H), 2.43 (m, 1H), 2.77 (m, 1H), 4.15 (m, 1H), 4.48 (s, 1H), 7.33 (d, 2H, *J* = 7.94 Hz), 7.60 (d, 2H, *J* = 7.94 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.69, 14.73, 20.73, 22.10, 23.29, 23.81, 25.53, 26.41, 26.56, 28.99, 32.41, 35.14, 62.52, 70.10, 72.88, 73.04, 126.15, 130.68, 140.93, 142.78; Calcd. for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; S, 10.82; Found: C, 68.92; H, 9.47; S, 10.83.

(2*RS*,3*S*)-2-[(*RS*)-*p*-Toluenesulfinyl]-3-decanol 6i. R_f 0.32 (EtOAc/hexane 1/1); oil; 80% yield; IR (neat, cm^{-1}): 3443, 2952, 1044; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86-1.40 (m, 18H), 2.41 (s, 1.5H), 2.42 (s, 1.5H), 3.12-3.21 (m,1H), 3.36-3.41 (m, 1H), 3.50 (s, 1H), 7.33 (d, 2H, *J* = 7.94 Hz), 7.60 (d, 2H, *J* = 8.24 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.54, 21.89, 23.05, 25.25, 29.66, 29.81, 30.09, 30.13, 32.19, 61.54, 64.21, 79.58, 80.11, 124.46, 125.86, 140.85, 142.65; Calcd. for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52; S, 10.82; Found: C, 68.84; H, 9.51; S, 10.78.

(4*RS*,3*S*)-2-Methyl-4-[(*RS*)-*p*-toluenesulfinyl]-3-hexanol 6j. R_f 0.32 (EtOAc/hexane 1/1); mp 74-78 °C; 73% yield; IR (KBr, cm^{-1}): 3358, 3044, 1031; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87-1.05 (m, 9H), 1.24-1.78 (m, 2H), 1.92 (m, 1H), 2.43 (s, 3H), 2.85 (m, 1H), 4.04 (m, 1H), 4.45 (d, 1H, *J* = 3.05 Hz), 7.34 (d, 2H, *J* = 7.94 Hz), 7.62 (d, 2H, *J* = 8.24 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.04, 15.44, 20.57, 21.96, 30.46, 69.20, 75.70, 125.64, 130.24, 140.83, 142.52; Calcd. for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72; S, 12.61; Found: C, 66.20; H, 9.77; S, 12.57.

(4*RS*,3*S*)-2-Methyl-4-[(*RS*)-*p*-toluenesulfinyl]-3-heptanol 6k. R_f 0.33 (EtOAc/hexane 1/1); oil; 65% yield; IR (neat, cm^{-1}): 3374, 2958, 1022; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, 2.16H, *J* = 6.88 Hz), 0.88 (d, 3.84H, *J* = 6.6 Hz), 1.02 (d, 3H, *J* = 6.88 Hz), 1.24-1.60 (m, 5H), 1.91 (m, 1H), 2.43 (s, 3H), 2.85-2.89 (m, 0.48H), 3.97-4.02 (m, 1H), 4.46 (d, 0.52H, *J* = 3.03 Hz), 7.25-7.60 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.68, 15.58, 20.02, 20.57, 21.92, 28.90, 30.57, 68.04, 76.32, 125.28, 125.65, 129.82, 130.19, 140.34, 142.29; Calcd. for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01; S, 11.95; Found: C, 67.29; H, 9.12; S, 12.02.

(2*RS*,1*S*)-1-Cyclohexyl-2-[(*RS*)-*p*-toluenesulfinyl]-1-propanol 6l. R_f 0.38 (EtOAc/hexane 1/1); mp 85% yield; IR (KBr, cm^{-1}): 3310, 2925, 1022; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (d, 3H, *J* = 6.88 Hz), 1.02-1.80 (m, 11H), 2.42 (s, 3H), 2.87-3.02 (m, 1H), 3.58-3.66 (m, 1H), 3.82 (d, 0.5H), *J* = 9.08 Hz), 4.44 (d, 0.5H, *J* = 2.20 Hz), 7.33 (d, 2H, *J* = 7.94 Hz), 7.60 (d, 2H, *J* = 8.24 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.82, 19.80, 21.95, 24.88, 25.97, 26.54, 26.68, 27.01, 30.45, 40.69, 62.91, 124.92, 124.99, 126.11, 129.93, 130.06, 130.16, 138.85, 142.61; Calcd. for $C_{16}H_{24}O_2S$: C, 68.53; H, 8.63; S, 11.43; Found: C, 68.57; H, 8.62; S, 11.40.

(2*RS*,1*S*)-1-Cyclohexyl-2-[(*RS*)-*p*-toluenesulfinyl]-1-pentanol 6m. R_f 0.47 (EtOAc/hexane 1/1); oil; 74% yield; IR (neat, cm^{-1}): 3376, 2967, 1033; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.81-1.73 (m, 18H), 2.43 (s, 3H), 2.92 (m, 1H), 3.93 (m, 1H), 4.31 (d, 1H, *J* = 3.7 Hz), 7.33 (d, 2H, *J* = 7.94 Hz), 7.60 (d, 2H, *J* = 8.24 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.85, 20.52, 26.96, 26.75, 26.97, 26.75, 26.97, 27.17, 29.53, 30.93, 41.14, 67.61, 126.08, 130.67, 141.05, 142.66; Calcd. for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15; S, 10.39; Found: C, 70.12; H, 9.12; S, 10.41.

Preparation of 2 by desufurization of 6. General procedure. According to the literature procedure,[14] a solution of each of **7c** and **8-10** (2 mmol) in anhydrous methanol (10 mL) was added to a suspension of Raney-Ni (*ca* 0.3 g) in anhydrous methanol. After the mixture was stirred for 6 h at room temperature, The Ni was removed by filtration on a celite short column. The filtrate was concentrated to give the product pheromones **1-4**, which were further purified by a flash chromatography on silica gel (230-400 mesh).

(*R*)-4-Methyl-2-pentanol (2a). R_f 0.42 (EtOAc/hexane 1/4); oil; 90% yield; IR (neat, cm^{-1}): 3432, 2936; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, 3H, *J* = 1.93 Hz), 0.91 (d, 3H, *J* = 1.93 Hz), 1.16 (d, 3H, *J* = 6.05 Hz), 1.21 (m, 1H), 1.41-1.46 (m, 1H), 1.69-1.76 (m, 1H), 2.88 (brs, 1H), 3.87 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.63, 23.30, 24.04, 24.97, 48.77, 65.93; GC analysis (column temperature: 40 °C, isothermal; carrier gas: He; head pressure: 13 psi, flow rate: 1 mL/min; detector: FID) using a G-TA column (Astec) showed it to be 98% ee [t_R(*R*) 7.12 min and t_R(*S*) 7.53 min].

(*R*)-2-Heptanol (2b). R_f 0.31 (EtOAc/hexane 1/4); oil; 89 % yield; IR (neat, cm^{-1}): 3344, 2956; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, 3H, *J* = 6.60 Hz), 1.19 (d, 3H, *J* = 6.05 Hz), 1.28-1.53 (m, 9H), 3.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.51, 23.07, 25.89, 32.23, 39.66, 68.51; $[\alpha]_D^{20}$ -9.49 (c 0.95, $CHCl_3$) *S*; {lit.[17] $[\alpha]_D^{22}$ +10.21 ($CHCl_3$), *R*, >99% ee}. GC analysis (column temperature: 40 °C, isothermal; carrier gas: He; head pressure: 13 psi, flow rate: 1 mL/min; detector: FID) using a G-TA column (Astec) showed it to be 96% ee [t_R(*R*) 7.24 min and t_R(*S*) 7.69 min].

(*R*)-2-Nonanol (2c). R_f 0.47 (EtOAc/hexane 1/4); oil; 93%

yield; IR (neat, cm^{-1}): 3394, 2961; ^1H NMR (200 MHz, $CDCl_3$) 0.88 (t, 3H, J = 5.80 Hz), 1.07-1.46 (m, 16H), 3.79 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.73, 23.31, 24.12, 26.44, 29.94, 30.28, 32.48, 40.05, 68.84; $[\alpha]_D^{20}$ -6.95 (c 1.1, $CHCl_3$) *S*; {lit.[17] $[\alpha]_D^{22}$ +7.96 ($CHCl_3$), *R*, >98% ee}. GC analysis of its acetate (column temperature: 130 °C, isothermal; carrier gas: He; detector: FID) using a β-Dex column (Supelco) showed it to be 96% ee [t_R(*S*) 21.07 min and t_R(*R*) 22.20 min].

(*R*)-1-Cyclohexylethanol (2d). R_f 0.29 (EtOAc/hexane 1/4); oil; 95% yield; IR (neat, cm^{-1}): 3402, 2925; ^1H NMR (200 MHz, $CDCl_3$) δ 0.86-1.88 (m, 15H), 3.55 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.00, 26.78, 26.87, 27.16, 29.01, 29.34, 45.77, 72.88; $[\alpha]_D^{20}$ +11.59 (*c* 2.23, CCl_4) as its acetate, *S* {lit.[9] $[\alpha]_D^{20}$ +10.6 (*c* 2.23, CCl_4) *R*, 97.9% ee}. GC analysis (column temperature: 75 °C, isothermal; carrier gas: He; detector: FID) using a α-Dex column (Supelco) showed it to be 99% ee [t_R(*R*) 43.99 min and t_R(*S*) 45.54 min].

(*R*)-5-Decanol (2h). R_f 0.42 (EtOAc/hexane 1/4); oil; 91 % yield; IR (neat, cm^{-1}): 3352, 2930; ^1H NMR (200 MHz, $CDCl_3$) δ 0.89-1.76 (m, 21H), 3.58 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.71, 23.30, 23.42, 25.98, 28.50, 32.58, 27.83, 38.10, 72.67; $[\alpha]_D^{20}$ -3.17 (*c* 0.4, CCl_4), probably *S* by analogy based on the sign of optical rotation values of its analogues; HPLC analysis of its benzoate using a Chiralpak-OT column (Daicel) (eluent: MeOH; flow rate: 0.3 mL/min; detector: 254 nm) showed it to be 97% ee [t_R(*R*) 22.65 min and t_R(*S*) 27.71 min].

(*R*)-3-Decanol (2i). R_f 0.43 (EtOAc/hexane 1/4); oil; 90% yield; IR (neat, cm^{-1}): 3352, 2958; ^1H NMR (200 MHz, $CDCl_3$) δ 0.85-1.05 (m, 6H), 1.28-1.59 (m, 15H), 3.52 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.51, 14.73, 23.31, 25.33, 29.96, 30.34, 30.80, 32.50, 37.62, 74.01; $[\alpha]_D^{20}$ -8.29 (*c* 0.59, $CHCl_3$), probably *S* by analogy based on the sign of optical rotation values of its analogues; GC analysis of its acetate (column temperature: 130 °C, isothermal; carrier gas: He; detector: FID) using a β-Dex column (Supelco) showed it to be 96% ee [t_R(*S*) 27.34 min and t_R(*R*) 28.39 min].

(*R*)-2-Methyl-3-hexanol (2j). R_f 0.53 (EtOAc/hexane 1/4); oil; 92% yield; IR (neat, cm^{-1}): 3355,2933; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (d, 3H, J = 2.40 Hz), 0.93 (d, 3H, J = 2.40 Hz), 1.30-1.70 (m, 9H), 3.37 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.80, 17.71, 19.48, 19.84, 34.13, 36.96, 36.98; $[\alpha]_D^{20}$ +28.2 (*c* 0.95, $CHCl_3$), *S* {lit.[18] $[\alpha]_D^{20}$ -16.8 (*c* 0.34, $CHCl_3$) *S*, 54% ee}; GC analysis (column temperature: 95 °C, isothermal; carrier gas: He; detector: FID) using a β-Dex column (Supelco) showed it to be 97% ee [t_R(*S*) 14.40 min and t_R(*R*) 14.96 min].

(*R*)-2-Methyl-3-heptanol (2k). R_f 0.56 (EtOAc/hexane 1/4); oil; 90% yield; IR (neat, cm^{-1}): 3362, 2958; ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (d, 3H, J = 2.44 Hz), 0.93 (d, 3H, J = 2.75 Hz), 1.31-1.74 (m, 11H), 3.36 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.01, 17.98, 19.80, 23.73, 29.18, 34.38, 34.79; $[\alpha]_D^{20}$ +25.52 (*c* 1.15, EtOH), *R* {lit.[19] $[\alpha]_D$ -8.86 (*c* 1.06, EtOH) *S*, 36% ee}; GC analysis (column temperature: 95 °C, isothermal; carrier gas: He; detector: FID) using a β-Dex column (Supelco) showed it to be 97% ee [t_R(*S*) 29.55 min and t_R(*R*) 30.37 min].

(*R*)-1-Cyclohexyl-1-propanol (2l). R_f 0.53 (EtOAc/hexane 1/4); oil; 92% yield; IR (neat, cm^{-1}): 3402, 2925; ^1H NMR (300 MHz, $CDCl_3$) δ 0.93-1.82 (m, 17H), 3.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.57, 26.74, 27.02, 28.06, 28.26, 29.63, 29.92, 43.41, 77.90; $[\alpha]_D^{20}$ +7.2 (*c* 0.68, $CHCl_3$), *S* {lit.[20] $[\alpha]_D^{20}$ +7.1 (*c* 0.7, $CHCl_3$) *R*, 99% ee}. GC analysis (column temperature: 85 °C, isothermal; carrier gas: He; detector: FID) using a a-Dex column (Supelco) showed it to be 99% ee [t_R(*R*) 44.61 min and t_R(*S*) 46.41 min].

(*R*)-1-Cyclohexyl-1-butanol (2m). R_f 0.47 (EtOAc/hexane 1/4); oil; 95% yield; IR (neat, cm^{-1}): 3341, 2926; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88-1.78 (m, 21H), 3.35 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.72, 23.46, 26.88, 27.05, 27.23, 28.35, 28.79, 29.94, 34.47, 44.23, 76.87; $[\alpha]_D^{20}$ +14.29 (*c* 1.93, $CHCl_3$), *S* {lit.[21] $[\alpha]_D^{20}$ -10.9 (*c* 1.8, $CHCl_3$) *R*, 72% ee}. GC analysis (column temperature: 125 °C, isothermal; carrier gas: He; detector: FID) using a β-Dex column (Supelco) showed it to be 99% ee [t_R(*S*) 91.62 min and t_R(*R*) 93.42 min]. Using the same methodology, **2e** with 98% ee, **2f** with 99% ee and **2g** with 96% ee were prepared.[12]

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